

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11) EP 0 892 979 B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention  
of the grant of the patent:

21.05.2003 Bulletin 2003/21

(51) Int Cl. 7: H01B 3/44

(21) Application number: 97917761.5

(86) International application number:  
PCT/US97/05297

(22) Date of filing: 01.04.1997

(87) International publication number:  
WO 97/038424 (16.10.1997 Gazette 1997/44)

### (54) ETHYLENE POLYMER COMPOSITION FOR CABLE APPLICATIONS

ETHYLENPOLYMER-ZUSAMMENSETZUNG FÜR ELECTRISCHE KABEL

COMPOSITION A BASE DE POLYMERES D'ETHYLENE POUR CABLES

(84) Designated Contracting States:

AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC  
NL PT SE

• MCADA, Richard, B.

Lake Jackson, TX 77566 (US)

(30) Priority: 10.04.1996 US 631320

(74) Representative:

Böhm, Brigitte, Dipl.-Chem. Dr. et al  
Weickmann & Weickmann  
Patentanwälte  
Postfach 86 08 20  
81635 München (DE)

(43) Date of publication of application:

27.01.1999 Bulletin 1999/04

(56) References cited:

-EP-A- 0 572 034 WO-A-93/13143  
WO-A-94/06858 WO-A-94/06859  
WO-A-94/17112 US-A- 3 674 915

(73) Proprietor: THE DOW CHEMICAL COMPANY

Midland, Michigan 48674 (US)

#### Remarks:

The file contains technical information submitted  
after the application was filed and not included in this  
specification

(72) Inventors:

- KALE, Lawrence, T.  
Lake Jackson, TX 77566 (US)
- IACCINO, Trudy, L.  
Friendswood, TX 77546 (US)
- BOW, Kenneth, E.  
Westerville, OH 43081 (US)

EP 0 892 979 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

**Description**

[0001] The present invention relates to cable applications, such as a coating on a fiber optical cable, coaxial cable, or telecommunications cable, comprising a layer of a specific polyethylene composition. More specifically, the polyethylene composition used in the cable of the present invention comprises a particular type of ethylene / $\alpha$ -olefin interpolymer, especially a homogeneously branched ethylene/ $\alpha$ -olefin interpolymer, and most preferably a homogeneously branched substantially linear ethylene/ $\alpha$ -olefin interpolymer; and a heterogeneously branched ethylene/ $\alpha$ -olefin interpolymer (or linear ethylene homopolymer). The cable of the present invention may have good mechanical properties such as abrasion resistance and flexibility, and good processability, moreover, may be less environmentally harmful (as compared with polyvinyl-chloride (PVC) based cables) when disposed.

[0002] Various types of thermoplastic polymer have been used for wire and cable jacketing applications. Especially, polymer compositions based on ethylene homopolymer via high pressure polymerization processes (low density polyethylene (LDPE)), and polyvinyl-chloride (PVC) have been used conventionally.

[0003] Various mechanical properties are desired for the cable jacketing application, for example, mechanical properties such as abrasion resistance, flexibility and reduced notch sensitivity are highly required. Moreover, good processability is also required for production efficiency and good appearance or quality of produced cable.

[0004] However, the above resins (that is LDPE, PVC) have several deficiencies. For example, LDPE may be acceptably flexible (that is low stiffness) but very often has low abuse resistance; moreover, since PVC contains chlorine, PVC-based cables release environmentally harmful gas such as hydrochloride gas when combusted. Furthermore, considering environmental adaptability, polymers such as PVC, especially those containing lead stabilizers, tend to release environmental harmful materials (for example, lead leached into ground water) when combusted or landfilled and should be avoided for this application. In addition, when the plasticizers leach out of a PVC formulation, the cable becomes brittle which leads to premature failure.

[0005] Linear polyethylene has also been used as a layer in a cable application, but these linear polyethylene polymers do not have adequate abuse resistance in combination with the necessary flexibility; that is, to increase abuse resistance in a linear polyethylene, one merely has to increase the density of the polyethylene, however raising the density reduces the flexibility. Reduced flexibility hampers installation of the cable, especially where the cable must be routed through numerous bends and twists/turns. Jacket or sheath damage resulting from poor flexibility usually results in cable failure.

[0006] In view of the above deficiencies, a resin composition which satisfies the above various mechanical properties, processability and environmental adaptability has been long awaited.

[0007] One aspect of the present invention is a cable of categories 1, 2 or 3 as defined by ASTM D 1248, comprising a jacket layer comprising a polyethylene composition, characterized in that the polyethylene composition comprises:

(A) from 25 to 45 percent by weight of the total composition of at least one homogeneously branched ethylene/ $\alpha$ -olefin interpolymer having:

- (i) a density from 0.89 g/cm<sup>3</sup> to 0.94 g/cm<sup>3</sup>,
- (ii) a molecular weight distribution (Mw/Mn) from 1.8 to less than 3.5,
- (iii) a melt index, I<sub>2</sub>, from 0.001 g/10 min. to less than 0.5 g/10 min., and
- (iv) a CDBI greater than 50 percent,

(B) at least 5 percent by weight of the total composition of at least one heterogeneously branched ethylene interpolymer or linear ethylene homopolymer having a density from 0.9 g/cm<sup>3</sup> to 0.965 g/cm<sup>3</sup>,

wherein the final melt index, I<sub>2</sub>, of the polyethylene composition in the cable jacket is in the range from 1 to 50 g/10 minutes, the polyethylene composition has a density of 0.945 g/cm<sup>3</sup> or more, and the cable jacket has a strain hardening modulus, G<sub>p</sub>, greater than 1.6 MPa wherein G<sub>p</sub> is calculated according to the following equation:

$$G_p = \frac{\sigma_{dr} \lambda_n - \sigma_{dr}}{\lambda_n^2 - \frac{1}{\lambda_n}}$$

wherein  $\lambda_n$  and  $\sigma_{dr}$  represent the natural draw ratio and engineering draw stress, respectively, and a reduced notch sensitivity as indicated for a notched cable jacket comprising a polyethylene composition and having a thickness from 2.03 to 2.29 mm (80-90 mil) taken in a circumferential direction by less than 55% loss of elongation compared to an unnotched cable jacket sample from said cable, as measured in accordance with ASTM D 638 at 23.9°C using a die

EP 0 892 979 B1

V (5) with a 2.5 cm jaw separation and pulling at a rate of 5.08 cm per minute.

[0008] Most preferably, the cable comprises a layer of a polyethylene composition characterized in that the polyethylene composition comprises 40 percent (by weight of the total composition) of the at least one first polymer which is characterized as having:

- 5 (I) a density from 0.91 to 0.92 g/cm<sup>3</sup>,
- (II) a molecular weight distribution ( $M_w/M_n$ ) of 2,
- (III) a melt index ( $I_2$ ) of 0.1 g/10 min., and
- (IV) a CDBI greater than 50 percent; and

10 about 60 percent (by weight of the total composition) of the at least one second polymer which is characterized as having heterogeneously branched ethylene/ $\alpha$ -olefin interpolymer:

- 15 (I) a density of 0.96 g/cm<sup>3</sup>,
- (II) a melt index ( $I_2$ ) of 6 g/10 min., and
- (III) a CDBI less than 50 percent.

[0009] Another aspect of the present invention is a cable jacket comprising the polyethylene composition of the invention which has at least 10 percent, preferably at least 20 percent, more flexibility than a cable made using conventional heterogeneous linear ethylene polymer having about the same density as the inventive polyethylene composition.

20 [0010] Yet another aspect of the invention is a cable comprising a thermoplastic cable jacket having a thickness from 80 to 90 mils (2.0 to 2.3 mm) in contact with a metal shield creating a notch in said jacket, wherein a sample of said notched jacket taken in a circumferential direction, in accordance with ASTM D 638, has less than 55 percent loss of elongation than an un-notched cable jacket sample from said cable.

25 [0011] Still another aspect of the invention is a cable comprising a thermoplastic ethylene polymer cable jacket composition, wherein a plaque having a single notch, a thickness from 70 to 80 mils (1.8 to 2.0 mm) made from said jacket composition has at least 100 percent, preferably at least 200 percent, more preferably at least 300 percent, especially at least 400 percent, and most especially at least 500 percent, ultimate tensile elongation, wherein the notch has a depth of at least 10 mils (0.25 mm), a radius from 0.275 mm to 0.55 mm, preferably 0.3 mm to 0.525 mm, and especially from 0.38 mm to 0.51 mm, and wherein said ethylene polymer composition has a density of at least 0.945 g/cm<sup>3</sup>.

30 [0012] In still another aspect, the invention is a cable comprising at least one layer of a thermoplastic polymer, especially a polyethylene polymer composition of the invention, wherein the thermoplastic polymer has a strain hardening modulus,  $G_p$ , greater than 1.6 MPa, preferably greater than 1.7 MPa, especially greater than 1.8 MPa, and can be as high as 2 MPa, wherein  $G_p$  is calculated according to the following equations:

$$(I) \quad \sigma_t = \sigma_{Eng} \lambda$$

$$40 (II) \quad G_p = \frac{\sigma_{dr} \lambda_n - \sigma_{dr}}{\lambda_n^2 - \frac{1}{\lambda_n}}$$

$$45 (III) \quad G_p = \frac{\rho RT}{M_e}$$

[0013] The strain hardening modulus ( $G_p$ ) is calculated from the conventional tensile stress-strain curve using the theory of rubber elasticity. More specifically, the true stress,  $\sigma_t$ , is calculated from the engineering stress,  $\sigma_{Eng}$ , and draw ratio,  $\lambda$ , as shown in Equation (I). For cable jacket resins, Equation (II) was used to calculate the strain hardening modulus, where  $\lambda_n$  and  $\sigma_{dr}$  represent the natural draw ratio and engineering draw stress, respectively. The natural draw ratio was determined by measuring the elongation of a grid pattern which was printed on the tensile dogbones. As shown in Equation (III), the strain hardening modulus is inversely related to the molecular weight between entanglements,  $M_e$ , that is, the molecular weight of the tie-molecules between crystalline domains and  $\rho$  is the density of the resin.

[0014] Figure 4, for example, shows strain hardening modulus as a function of density of the ethylene polymer composition. For examples E, En, A, and An, the strain hardening modulus relationship can be approximated by the following

equation:

$$(IV) \quad G_p = -98.57 + (208.89)(\rho) - (108.73)(\rho)^2$$

5 where  $\rho$  = density of the ethylene polymer composition (including carbon black in the density calculation if appropriate) and  $G_p$  is the strain hardening modulus. Note that polymers B and Bn fall above the line, which is believed to be attributed to higher levels of long chain branching (that is, the  $I_{10}/I_2$  melt flow ratio is higher for the homogeneous component for resin Bn than for the homogeneous component of resins En and/or An).

10 [0015] For comparative polymers J, D, I and G, the strain hardening modulus follows a different relationship described by equation (V):

$$(V) \quad G_p = -438.03 + (921.96)(\rho) - (483.46)(\rho)^2.$$

15 Note that the line for the comparative polymers is much lower than that for the polymer compositions of the invention. [0016] Preferably, the polyethylene composition used in the cable of the present invention is prepared by a process comprising the steps of:

- 20 (i) reacting by contacting ethylene and at least one  $\alpha$ -olefin under solution polymerization conditions in at least one reactor to produce a solution of the at least one first polymer which is a homogeneously branched ethylene/ $\alpha$ -olefin interpolymer, preferably a substantially linear ethylene/ $\alpha$ -olefin interpolymer,  
 (ii) reacting by contacting ethylene and at least one  $\alpha$ -olefin under solution polymerization conditions in at least one other reactor to produce a solution of the at least one second polymer which is a heterogeneously branched  
 25 ethylene polymer,  
 (iii) combining the solution prepared in steps (i) and (ii), and  
 (iv) removing the solvent from the polymer solution of step (iii) and recovering the polyethylene composition.

[0017] The cables of the present invention have good flexibility, mechanical properties and good processability, furthermore, are environmentally less harmful when disposed relative to cables comprising conventional PVC. An important aspect of the present invention is the fact that cables, where the outer cable jacket comprises the compositions disclosed in this invention, have improved flexibility relative to comparative cables where the jacket is produced from conventional heterogeneous linear low density polyethylenes (LLDPE). Cable flexibility is an important performance criteria, since more flexible cables are easier to install and bend around corners. Cable flexibility was measured by clamping a piece of cable horizontally in an Instron tensile machine and measuring the force required to deflect the cable in the upward direction. Lower deflection forces demonstrate improved flexibility, as shown in Figure 1. Cable jackets produced from the copolymers of this invention are preferably 10 percent more flexible, and more preferably 20 percent more flexible than comparative cables made using conventional heterogeneous linear low density ethylene polymers having about the same density (that is, the density of each polymer is within 10 percent of the other).

40 [0018] These and other embodiments are more fully described below, and in conjunction with the Figures, wherein:

FIG. 1 is a plot of deflection force (kg) versus cable deflection (mm) for example A and comparative example G; FIG. 2 is a plot of ultimate tensile elongation (percent) versus notch number in the test sample for example B and for comparative example G;

45 FIG. 3 is a plot of change in the relative tensile elongation versus temperature for example A and comparative example G;

FIG. 4 is a plot of strain hardening modulus (MPa) versus polymer and composition density for example polymers A, An, B, Bn, E, and En, and for comparative examples D, G, I and J;

FIG. 5 is a surface roughness scan of a cable jacket made from example B;

50 FIG. 6 is a surface roughness scan of a cable jacket made from comparative example G; and

FIG. 7 is a schematic representation, in perspective and partly broken away, showing one cable of the present invention.

[0019] The "substantially linear" ethylene/ $\alpha$ -olefin interpolymers useful in the present invention are not "linear" polymers in the traditional sense of the term, as used to describe linear low density polyethylene (Ziegler polymerized linear low density polyethylene (LLDPE)), nor are they highly branched polymers, as used to describe low density polyethylene (LDPE). The "substantially linear" ethylene/ $\alpha$ -olefin interpolymers have long chain branching, wherein the backbone is substituted with 0.01 long chain branches/1000 carbons to 3 long chain branches/1000 carbons, more

preferably from 0.01 long chain branches/1000 carbons to 1 long chain branches/1000 carbons, and especially from 0.05 long chain branches/1000 carbons to 1 long chain branches/1000 carbons. Note that the long chain branches are not the same as the short chain branches resulting from incorporation of the comonomer. Thus, for an ethylene/1-octene copolymer, the short chain branches are six carbons in length, while the long chain branches for such a substantially linear ethylene/1-octene copolymer are at least seven carbons in length, but usually much longer than seven carbons.

**[0020]** The substantially linear ethylene/α-olefin interpolymers of the present Invention are herein defined as in U.S. patent 5,272,236 (Lai et al.) and 5,278,272 (Lai et al.). Long chain branching is defined herein as a chain length of at least 7 carbons, above which the length cannot be distinguished using  $^{13}\text{C}$  nuclear magnetic resonance (NMR) spectroscopy. The long chain branch can be as long as the length of the polymer backbone.

**[0021]** For ethylene homopolymers and ethylene/C<sub>3</sub>-C<sub>7</sub> alpha-olefin copolymers, long chain branching can be determined by  $^{13}\text{C}$  NMR spectroscopy and can be quantified using the method of Randall (Rev. Macromol. Chem. Phys., C29 (2&3), p. 285-297). Union Carbide, in EP 0659773 A1, used a 1990 paper (Mirabella et al.) to quantify long chain branching. Exxon used "viscous energy of activation" to quantify long chain branching in PCT Publication WO 94/07930.

**[0022]** Both the homogeneous linear and the substantially linear ethylene/α-olefin interpolymers useful for forming the compositions of the present invention are those in which the comonomer is randomly distributed within a given interpolymer molecule and wherein substantially all of the interpolymer molecules have the same ethylene / comonomer ratio within that interpolymer, as described in USP 3,645,992 (Elston). The homogeneity of the interpolymers is typically described by the SCBDI (Short Chain Branching Distribution Index) or CDBI (Composition Distribution Branch/Breadth Index) and is defined as the weight percent of the polymer molecules having a comonomer content within 50 percent

of the median total molar comonomer content. The CDBI of a polymer is readily calculated from data obtained from techniques known in the art, such as, for example, temperature rising elution fractionation (abbreviated herein as "TREF") as described, for example, in Wild et al, Journal of Polymer Science, Poly. Phys. Ed., Vol. 20, p 41 (1982), in U.S. patent 4,798,081 (Hazlitt et al.), or in U.S. patent 5,089,321 (Chum et al.). The SCBDI or CDBI for the homogeneous ethylene/α-olefin interpolymer used in the present invention is greater than 50 percent, more preferably greater

than about 70 percent, and especially greater than about 90 percent. The homogeneous ethylene/α-olefin interpolymers used in the present invention essentially lack a linear polymer fraction which is measurable as "high density" fraction by the TREF technique (that is homogeneously branched ethylene/α-olefin interpolymers do not contain a polymer fraction with a degree of branching less than or equal to 1 methyl/1000 carbons). For homogeneous linear or substantially linear ethylene/α-olefin interpolymers, especially ethylene/1-octene copolymers, having a density from about 0.88 g/cm<sup>3</sup> and higher, these interpolymers also do not contain any highly short chain branched fraction (that is the homogeneously branched ethylene/α-olefin polymers do not contain a polymer fraction with a degree of branching equal to or more than about 30 methyls/1000 carbons).

**[0023]** The homogeneous linear or substantially linear ethylene/α-olefin interpolymer for use in the present invention typically are interpolymers of ethylene and at least one C<sub>3</sub>-C<sub>20</sub> α-olefin and/or C<sub>4</sub>-C<sub>18</sub> diolefin, preferably interpolymers of ethylene and C<sub>3</sub>-C<sub>20</sub> α-olefins, more preferably a copolymer of ethylene and a C<sub>4</sub>-C<sub>8</sub> α-olefin, most preferably a copolymer of ethylene and 1-octene. The term interpolymer is used herein to indicate a copolymer, or a terpolymer, or the like. That is, at least one other comonomer is polymerized with ethylene to make the interpolymer. Ethylene polymerized with two or more comonomers can also be used to make the homogeneously branched substantially linear interpolymers useful in this invention. Preferred comonomers include the C<sub>3</sub>-C<sub>20</sub> α-olefins, especially propene, isobutylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-nonene, and 1-decene, more preferably 1-butene, 1-hexene, 4-methyl-1-pentane and 1-octane.

**[0024]** The homogeneously branched linear and substantially linear ethylene/α-olefin interpolymers used in the present invention have a single melting peak, as determined using differential scanning calorimetry (DSC) using a second heat and a scanning range from -30°C to 140°C at 10°C/minute, as opposed to traditional heterogeneously branched Ziegler polymerized ethylene/α-olefin copolymers having two or more melting peaks, as determined using DSC.

**[0025]** The density of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers (as measured in accordance with ASTM D-792) for use in the present invention is generally from 0.89 g/cm<sup>3</sup> to 0.94 g/cm<sup>3</sup>, and preferably from 0.9 g/cm<sup>3</sup> to 0.935 g/cm<sup>3</sup>.

**[0026]** The amount of the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymer incorporated into the composition used in the cable of the present invention varies depending upon the heterogeneously branched ethylene polymer to which it is combined. However, preferably from 5 to 95 percent, more preferably from 20 to 80 percent, most preferably from 25 to 45 percent (by weight of the total composition ) of the homogeneous linear or substantially linear ethylene/α-olefin polymer may be incorporated in the polyethylene composition for use in the cable of the present invention.

**[0027]** The molecular weight of the homogeneously branched linear or substantially linear ethylene/α-olefin polymer for use in the present invention is conveniently indicated using melt index measurement according to ASTM D-1238, condition 190°C/2.16 kg (formerly known as "condition (E)", and also known as I<sub>2</sub>). Melt index is inversely proportional

to the molecular weight of the polymer; although, the relationship is not linear. The homogeneously branched linear or substantially linear ethylene/α-olefin interpolymers useful herein will generally have a melt index of at least 0.001 grams/10 minutes (g/10 min.), and preferably at least 0.03 g/10 min. The homogeneously branched linear or substantially linear ethylene/α-olefin interpolymer will have a melt index of less than 0.5 g/10 min.

[0028] Another measurement useful in characterizing the molecular weight of the homogeneously branched substantially linear ethylene/α-olefin interpolymers is conveniently indicated in melt index measurement according to ASTM D-1238, condition 190°C/10 kg (formerly known as "Condition (N)" and also known as  $I_{10}$ ). The ratio of the  $I_{10}$  and  $I_2$  melt index is the melt flow ratio and is designated as  $I_{10}/I_2$ . Generally, the  $I_{10}/I_2$  ratio for the homogeneously branched linear ethylene/α-olefin interpolymers is about 5.6. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers used in the polyethylene composition of the present invention, the  $I_{10}/I_2$  ratio indicates the degree of long chain branching, that is, the higher the  $I_{10}/I_2$  ratio, the more long chain branching in the interpolymer. Generally, the  $I_{10}/I_2$  ratio of the homogeneously branched substantially linear ethylene/α-olefin interpolymers is at least 6, preferably at least 7, especially at least 8 or above, and can be as high as 20. For the homogeneously branched substantially linear ethylene/α-olefin interpolymers, the higher the  $I_{10}/I_2$  ratio, the better the processability.

[0029] The molecular weight distribution of the substantially linear ethylene interpolymer in the present invention may be analyzed by gel permeation chromatography (GPC) on a Waters 150°C high temperature chromatographic unit equipped with three mixed porosity columns (Polymer Laboratones  $10^3$ ,  $10^4$ ,  $10^5$  and  $10^6$ ), operating at a system temperature of 140°C. The solvent is 1,2,4-trichlorobenzene, from which 0.3 percent by weight solutions of the samples are prepared for injection. The flow rate is 1.0 mL/minutes and the injection size is 100 microliters. A differential refractometer is being used as the detector.

[0030] The molecular weight determination is deducted by using narrow molecular weight distribution polystyrene standards (from Polymer Laboratories) in conjunction with their elution columns. The equivalent polyethylene molecular weights are determined by using appropriate Mark-Houwink coefficient for polyethylene and polystyrene (as described by Williams and Ward in Journal of Polymer Science, Polymer Letters, Vol. 6, (621) 1968, incorporated herein by reference) to derive the following equation:

$$M_{\text{polyethylene}} = a^*(M_{\text{polystyrene}})^b$$

[0031] In this equation,  $a=0.4316$  and  $b=1.0$ . Weight average molecular weight,  $M_w$ , is calculated in the usual manner according to the following formula:  $M_w = \sum w_i M_i$ , where  $w_i$  and  $M_i$  are the weight fraction and molecular weight, respectively, of the  $i^{\text{th}}$  fraction eluting from the GPC column.

[0032] For the homogeneously branched linear and substantially linear ethylene/α-olefin interpolymers, the molecular weight distribution ( $M_w/M_n$ ) is from 1.8 to less than 3.5, preferably from 1.8 to 2.8, more preferably from 1.89 to 2.2 and especially about 2.

[0033] The ethylene polymer to be combined with the homogeneously branched linear or substantially linear ethylene/α-olefin interpolymer is a heterogeneously branched ethylene polymer, preferably a heterogeneously branched (for example, Ziegler polymerized) interpolymer of ethylene with at least one  $C_3-C_{20}$  α-olefin (for example, linear low density polyethylene (LLDPE)).

[0034] Heterogeneously branched ethylene/α-olefin interpolymers differ from the homogeneously branched ethylene/α-olefin interpolymers primarily in their branching distribution. For example, heterogeneously branched LLDPE polymers have a distribution of branching, including a highly short chain branched portion (similar to a very low density polyethylene), a medium short chain branched portion (similar to linear low density polyethylene) and often a linear (that is, non-short chain branched) portion. The amount of each of these fractions varies depending upon the whole polymer properties desired. For example, linear homopolymer polyethylene has no short chain branching. A very low density heterogeneous polyethylene having a density from 0.89 g/cm<sup>3</sup> to 0.915 g/cm<sup>3</sup> (such as Attane™ copolymers, sold by The Dow Chemical Company and Flexomer™ sold by Union Carbide Corporation) has a higher percentage of the highly short chain branched fraction, thus lowering the density of the whole polymer.

[0035] Preferably, the heterogeneously branched ethylene polymer is a heterogeneously branched ethylene/α-olefin interpolymer, most preferably Ziegler polymerized ethylene/α-olefin copolymer. The α-olefin for such ethylene interpolymer may include α-olefin having 3 to 30 carbon atoms, more preferably an α-olefin having 4 to 8 carbon atoms, most preferably 1-octene.

[0036] More preferably, the heterogeneously branched ethylene polymer is a copolymer of ethylene with a  $C_3-C_{20}$  α-olefin, wherein the copolymer has:

- (i) a density from 0.9 g/cm<sup>3</sup> to 0.965 g/cm<sup>3</sup>,
- (ii) a melt index ( $I_2$ ) from about 0.1 g/10 min. to about 500 g/10min.

[0037] The heterogeneously branched ethylene/α-olefin interpolymers and/or copolymers, especially those having a density of less than 0.95 g/cm<sup>3</sup>, (excluding, of course, ethylene homopolymers having a single melting peak) also have at least two melting peaks as determined using Differential Scanning Calorimetry (DSC), using the same scanning rate and temperature range described earlier herein.

5 [0038] The compositions disclosed herein can be formed by any convenient method, including dry blending the individual components and subsequently melt mixing or by pre-melt mixing in a separate extruder (for example, a Banbury mixer, a Haake mixer, A Brabender internal mixer, or a twin screw extruder).

10 [0039] Another technique for making the compositions *in-situ* is disclosed in PCT applications WO 92/11269 and WO 94/01052. PCT applications WO 92/11269 and WO 94/01052 describe, *inter alia*, interpolymerizations of ethylene and C<sub>3</sub>-C<sub>20</sub> α-olefins using a homogeneous catalyst in at least one reactor and a heterogeneous catalyst in at least one other reactor. The reactors can be operated in series or in parallel.

15 [0040] A preferred density of the polyethylene composition used for the cable of the present invention may depend upon desired stiffness of the finished cable. However, typical densities will preferably be from 0.91 to 0.96 g/cm<sup>3</sup>, more preferably from 0.92 to 0.96 g/cm<sup>3</sup>.

20 [0041] A preferred melt index (that is I<sub>2</sub>) of the polyethylene composition disclosed herein may depend upon process conditions and desired physical properties. However, generally, the melt index of the polyethylene composition disclosed herein may be from 1 to 50 g/10 minutes for all categories of cable, preferably greater than 1 to 10 g/10 minutes for category three (3), and preferably greater than 10 to 25 g/10 minutes for category two (2), and greater than 25 g/10 minutes for category one (1). These general categories are found in ASTM D 1248, and are also included in the Standard Specifications for Plastic, Molding and Extrusion. However, if the I<sub>2</sub> of the polyethylene composition disclosed herein is lower than about 0.1 g/10 minutes, the polyethylene composition is often difficult to extrude and may cause melt fracture on the surface of the finished cable. Likewise, if the I<sub>2</sub> of the polyethylene composition disclosed herein is higher than the above ranges, the molten polymer tends to have a low melt viscosity and melt tension, thus may be difficult to fabricate into the desired cable.

25 [0042] The I<sub>10</sub>/I<sub>2</sub> of the polyethylene composition disclosed herein may be preferably from 7 to 16, more preferably from 9 to 14, most preferably from 10 to 13. If the I<sub>10</sub>/I<sub>2</sub> of the polyethylene polymer disclosed herein is lower than the above range, surface quality of the finished cable tends to be deteriorated, and processability of the cable may become unacceptably low.

30 [0043] The resin composition of the present invention may comprise any known additives and/or fillers to the extent that they do not interfere with the enhanced formulation properties discovered by Applicants. Any additives commonly employed in polyolefin compositions, for example, cross-linking agents, antioxidants (for example, hindered phenolics (for example, Irganox™ 1010 made by Ciba Geigy Corp.), phosphites (for example, Irgafos™ 168 also by Ciba Geigy Corp.), flame retardants, heat stabilizers, ultra-violet absorbents, anti-static agents, slip agents, process aids, foaming agents, plasticizers, dyes, miscellaneous fillers such as clay and pigments can be included in the formulation. A preferable additive of the present invention may include, for example, carbon black, and an antioxidant such as Irganox™ 1010 and Irgafos™ 168.

35 [0044] The composition of the present invention may be further fabricated into desired cable of the present invention by using any known fabrication method. The composition of the present invention may be used not only for cable jacketing, but also cable insulation or any layer of a cable. For example, the composition described herein may be heated, melted, kneaded and extruded by a mono- or bi-axial extruder through an extrusion die such as a cross-head die so as to be applied onto a core substrate, and then it may be subjected to a cooling step, or the next coating step if desired. Multiple layers of polymers may be applied onto the core substrate if desired. The core substrate may comprise any known materials in the art, for example, control cables comprising any conductive material such as copper, and aluminum, insulating material such as low density polyethylene, polyvinyl-chloride, polyethylene compositions including compositions described herein, conductive or semiconductive shields such as aluminum, copper, and steel, usually in form of tape, foil, screen, net or any combinations thereof, and any reinforcement material.

40 [0045] Various cables and cable designs may include, as at least one layer, the polyethylene compositions disclosed herein. For example, USP 3,638,306 (Padowicz) shows a communications cable which has a water proof core of conductors and a sheath including an unsoldered steel layer. Figure 7 herein shows such a structure: the steel layer (1) is stretch-formed to attain a tightly registered longitudinal seam which eliminates the necessity of soldering or other means of mechanically joining the seam.

45 [0046] A cable 101 includes a plurality of conductors or conductor pairs 4 within a cable core 2. The conductors 4 are surrounded by and the interstitial spaces therebetween are filled with a waterproof filler material 6.

50 [0047] About core 2 is a core wrap 8 which may be a suitable plastic or other material. A binder can be placed around core wrap 8 to hold it in position about core 2, a layer of conductive metal is placed about the core. A thin aluminum layer 10 having a longitudinal seam 14 therein advantageously can be used for lightning protection and shielding. Longitudinal seam 14 is not required to be soldered or otherwise mechanically joined, a steel layer 20 having unsoldered overlapping edges 16 and 18 forming a longitudinal seam 17 is longitudinally wrapped about aluminum layer 10 to

provide protection from mechanical forces such as abrasion. The use of an unsoldered seam 17 for steel layer 20 is possible, since the cable core 2 is waterproof. Steel layer 20 and aluminum layer 10 advantageously can be transversely corrugated and meshed with each other to provide a more flexible sheath. Steel layer 20 is stretch-formed and cold-worked as it is wrapped about aluminum layer 10 and edges 16 and 18 are closely meshed to provide a tightly registered overlapping seam 17. The stretch-forming and cold-working insure that edges 16 and 18 retain their respective positions without the necessity for external holding forces after the forming forces have been removed. Thus, the tightly registered seam 17 is maintained. Edges 16 and 18 will retain their positions and maintain the tightly registered seam 17 even when cable 101 is wound on a reel. The outer or overlying edge 16 of steel layer 20 advantageously can be turned slightly inward toward core 2 to insure that no sharp edges are presented by steel layer 20.

[0048] Corrosion protection for steel layer 20 and added protection against water penetration are provided by hot-melt flooding each side of steel layer 20 with respective coatings 12 and 22 of a corrosionproof, waterproof material (such as a Pramacor™ Adhesive Polymer made by The Dow Chemical Company). This readily can be accomplished by drawing cable 101 through a bath of appropriate material as layer 20 is being applied. Coatings 12 and 22 advantageously might be the same material as is utilized for filler material 6. Protection against water penetration is obtained since coatings 12 and 22, respectively, fill all spaces between steel layer 20 and the adjacent layers 10 and jacket 24 of the cable sheath. Jacket 24 is desirably made using the ethylene polymer compositions disclosed herein. Seam 17 is also sealed against water ingress by coatings 12 and 22 being drawn into seam 17 by capillary action of the tightly registered seam. Added mechanical strength is also obtained from the adhesive forces of coatings 12 and 22 which tend to adhere steel layer 20 to adjacent layers 10 and jacket 24.

[0049] For added corrosion protection of layer 20 and for additional mechanical and moisture protection, an exterior ethylene polymer composition jacket 24 advantageously is extruded around the exterior surface of layer 20. Thus, the cable sheath comprising an aluminum layer 10, an unsoldered steel layer 20 and a thermoplastic layer or jacket 24 joined by corrosion coatings 12 and 22 provides mechanical, rodent, and waterproof protection at a cost substantially less than the sheaths of prior art cables. In Figure 7, various layers may comprise the ethylene polymer compositions disclosed herein, including jacket 24, layers 22, 12 and 8; further any or all of these layers may comprise the ethylene polymer compositions disclosed herein.

[0050] Other United States Patents disclosing useful cable structures enhanced by use of a layer comprising the polyethylene compositions layer of the present invention include US Patent 4,439,632 (Aloisio, Jr. et al.), US Patent 4,563,540 (Bohannon, Jr. et al.), US Patent 3,717,716 (Biskebom et al.), and US Patent 3,681,515 (Mildner).

[0051] The present invention will be more clearly understood with reference to the following examples.

#### Cable Example 1

[0052] A cable was produced by using polymer A which was an *in-situ* blend made according to PCT Publications WO 92/11269 and WO 94/01052, wherein 36 weight percent of the total composition of a homogeneously branched substantially linear ethylene/1-octene copolymer having a density of 0.915 g/cm<sup>3</sup> was made in a first reactor, and 64 weight percent of the total composition of a heterogeneously branched linear ethylene/1-octene copolymer having a density of 0.955 g/cm<sup>3</sup> was made in a second reactor. Polymer A had a melt index ( $I_2$ ) of 0.78 g/10 minutes,  $I_{10}/I_2$  of 11.9, a density of 0.958 g/cm<sup>3</sup> (note that polymer A contained 2.6 weight percent carbon black and 400 ppm of a fluoroelastomer) and 0.039 long chain branches/10,000 carbons (0.39 long chain branches/1000 carbons) as determined using a kinetic model, and a  $M_w/M_n$  of 7.5. The polymer was extruded onto a cable by using a cable manufacturing line equipped with an extruder having a diameter of 6.35 cm, length to diameter ratio of 20 to 1 with a 5 turn metering screw having a compression ratio of 3.66 to 1, with a crosshead die having a die diameter of 2.04 cm, die-tip inside diameter of 1.73 cm, a die gap of 0.318 cm, and 0 cm land length. The cable was produced by forming corrugated steel over a polyvinylchloride jacketed control cable and extruding the polymeric jacket over the steel sheath. The extruder speed was approximately 55 rpm and the cable line speed was held constant at 760 cm/minutes. The melt temperature was 232°C to 240°C using the following temperature profile: zone 1, 166°C; zone 2, 171°C; zone 3, 188°C; zone 4, 205°C; cross head, 219°C; die, 227°C. Pressure, amps, melt temperature and cable melt strength were evaluated subjectively (for example, the cable jackets did or did not have the required melt strength during extrusion as reported in Table 1). The surfaces of the cable jackets were evaluated visually and assigned a numerical surface rating, where the highest quality surface was given a rating of 100. The results are also reported in Table 1. The finished cable was subjected to physical properties test described below.

#### Cable Example 2

[0053] A cable was produced by using polymer B which was an *in-situ* blend made according to PCT Publications WO 92/11269 and WO 94/01052, wherein 41 weight percent of the total composition of a homogeneously branched substantially linear ethylene/1-octene copolymer having a density of 0.915 g/cm<sup>3</sup> was made in a first reactor, and 59

EP 0 892 979 B1

weight percent of the total composition of a heterogeneously branched linear polymer ethylene/1-octene copolymer having a density of 0.955 g/cm<sup>3</sup> was made in a second reactor. The polymer B had a melt index of 0.89 g/10minutes, I<sub>10</sub>/I<sub>2</sub> of 11.3, density of 0.957 g/cm<sup>3</sup> (note that polymer B contained 2.6 weight percent carbon black and 400 ppm of a fluoroelastomer), 0.18 long chain branches/10,000 carbon atoms (1.8 long chain branches/1000 carbon atoms) as calculated using a kinetic model, and molecular weight distribution (that is M<sub>w</sub>/M<sub>n</sub>) of 5.01. The polymer was extruded onto cable as described in Example 1. The finished cable was subjected to the physical property tests described below. Melt tension and cable surface rating were measured by the methods described in Example 1, and are reported in Table 1.

10 Cable Example 3

[0054] An cable is produced by using polymer C which was an *in-situ* blend ethylene/1-octene copolymer produced by the same process described in Example 1, having a melt index of 0.87 g/10minutes, I<sub>10</sub>/I<sub>2</sub> of 10.47 and density of 15 0.952 g/cm<sup>3</sup>(note that polymer C contained 2.6 weight percent carbon black and 400 ppm of a fluoroelastomer) and a M<sub>w</sub>/M<sub>n</sub> of 5.22. The polymer was extruded onto cable as described in Example 1. Surface rating is reported in Table 1. The finished cable was subjected to physical properties tests described below.

Comparative Cable Example 4

20 [0055] A cable was produced by using polymer D, which is a currently available polyethylene (for example UCC 8864 by Union Carbide) having melt index of 0.76 g/10minutes, I<sub>10</sub>/I<sub>2</sub> of 12.3, density of 0.942 g/cm<sup>3</sup>, and M<sub>w</sub>/M<sub>n</sub> of 3.7, and no long chain branching. Polymer D also contained 2.6 weight percent carbon black and about 400 ppm of a fluoroelastomer. The polymer was extruded onto cable as described in Example 1. Melt tension data and cable surface rating are reported in Table 1.

25 Cable Example 5

30 [0056] A cable was produced by using polymer E which was an *in-situ* blend ethylene/1-octene copolymer produced by the same process described in Example 1, having a melt index of 0.58 g/10minutes, I<sub>10</sub>/I<sub>2</sub> of 11.03, and density of 0.944 g/cm<sup>3</sup>, and M<sub>w</sub>/M<sub>n</sub> of 5.1. Polymer E also contained 2.6 weight percent carbon black and 400 ppm of a fluoroelastomer. The polymer was extruded onto cable as described in Example 1. Melt tension and surface rating are reported in Table 1. The finished cable was subjected to physical properties test described below.

35 Cable Example 6

40 [0057] A cable was produced by using polymer F which was an *in-situ* blend ethylene/1-octene copolymer produced by the same process described in Example 1, having a melt index of 0.88 g/10minutes, I<sub>10</sub>/I<sub>2</sub> of 10.13, density of 0.94 g/cm<sup>3</sup>, and a M<sub>w</sub>/M<sub>n</sub> of about 4.6. Polymer F contained 2.6 weight percent carbon black and 400 ppm of a fluoroelastomer. The polymer was extruded onto cable as described in Example 1 and subjected to physical properties tests described below. Melt tension and surface rating are reported in Table 1.

Comparative Cable Example 7

45 [0058] A cable was produced by using polymer G, which is a currently available polyethylene (for example UCC 3479 by Union Carbide) having melt index of 0.12 g/10minutes, I<sub>10</sub>/I<sub>2</sub> of 29.4, density of 0.958 g/cm<sup>3</sup>, M<sub>w</sub>/M<sub>n</sub> of 5.6, and no long chain branching. Polymer G contained 2.6 weight percent carbon black and about 400 ppm of a fluoroelastomer. The polymer was extruded onto cable as described in Example 1 and subjected to physical properties tests described below. Melt tension and surface rating are reported in Table 1.

50 Table 1

Resin*	Used to Make Cable	I <sub>2</sub> (g/10min.)	I <sub>10</sub> /I <sub>2</sub>	Density (g/cm <sup>3</sup> )	Visual Surface Rating	Melt Strength (cN)
Polymer A	Example 1	0.78	11.9	0.958	90	-
Polymer B	Example 2	0.89	11.3	0.957	100	3.69

\* All of these resins contained 2.6 wt percent carbon black and 400 ppm fluoroelastomer

## EP 0 892 979 B1

Table 1 (continued)

Resin*	Used to Make Cable	$I_2$ (g/10min.)	$I_{10}/I_2$	Density (g/cm <sup>3</sup> )	Visual Surface Rating	Melt Strength (cN)
5 Polymer C	Example 3	0.87	10.47	0.952	75	-
	Polymer D	0.76	12.26	0.942	95	6.57
10 Polymer E	Example 5	0.58	11.03	0.948	65	4.5
	Polymer F	0.88	10.13	0.940	70	4.2
Polymer G	Comp. Ex 7	0.12	29.4	0.958	80	7.1

\* All of these resins contained 2.6 wt percent carbon black and 400 ppm fluoroelastomer.

15 Surface Profilometry

[0059] The surface roughness of Example 2 and comparative Example 7 was quantified using surface profilometry. More specifically, the average surface roughness of these cables was measured using a Surftest 402 Surface Roughness Tester, produced by Mitutoyo. This analyzer computes various surface roughness parameters given a scan of the cable surface with a diamond tipped stylus. Surface roughness is quantified by the statistical parameter,  $R_a$ , known as the average roughness. This quantity is the arithmetic mean of all departures of the roughness profile from the average mean line as in Equation (V).

$$(V) \quad R_a = \frac{1}{N} \sum_{n=1}^N |f(x)|$$

25 where N is the number of digitized data points within the length of cable used for the measurement and  $f(x)$  is the vertical departure from the mean surface line at each data point.

[0060] The average roughness of Example 2 was  $28.0 \pm 1.4 \mu\text{in}$ . ( $0.71 \pm 0.036$  microns), while the average roughness of comparative example 7 was  $60.5 \pm 2.1 \mu\text{in}$  ( $1.54 \pm 0.053$  microns). The surface roughness of the copolymers described in this invention is less than half the roughness of the comparative sample. Typical profilometer traces from the surface of cable Example 2 and Example 7 are shown in Figures 5 and 6.

[0061] This surface roughness data is surprising, given the  $I_{10}/I_2$  values, for example, 11.3 for Example 2 and 29.4 for comparative Example 7. More specifically, it is well known that processability improves and surface roughness (melt fracture) decreases as  $I_{10}/I_2$  increases. In other words, the very smooth cables produced by the copolymers of this invention were surprising, given their relatively low  $I_{10}/I_2$  values.

35 Circumferential and Longitudinal Tensile Tests

40 [0062] Circumferential tensile samples were cut from the finished cables perpendicular to the cable axis with no metal seam impressions within gauge length. Longitudinal tensile samples were cut parallel to the cable axis with no metal seam impressions within gauge length. The tensile test was carried out according to ASTM D 638, using Die V (5) (for example microtensile), with a 2.54 cm jaw separation and pulling at 1.27 cm/minutes. The tensile strength data are reported in Table 2.

45 Table 2

Resin	Circumferential Tensiles			Longitudinal Tensiles		
	Yield (kg/cm <sup>2</sup> )	Ultimate		Yield (kg/cm <sup>2</sup> )	Ultimate	
	Stress (kg/cm <sup>2</sup> )	Elongation (percent)		Stress (kg/cm <sup>2</sup> )	Elongation (percent)	
Polymer A	125	144	380	127	178	510
Polymer B	117	158	450	122	186	525
Polymer C	134	201	540	137	204	565

Table 2 (continued)

Resin	Circumferential Tensiles			Longitudinal Tensiles		
	Yield (kg/cm <sup>2</sup> )	Ultimate		Yield (kg/cm <sup>2</sup> )	Ultimate	
	Stress (kg/cm <sup>2</sup> )	Elongation (percent)		Stress (kg/cm <sup>2</sup> )	Elongation (percent)	
Polymer G*	169	111	460	157	214	670
Polymer E	89	123	385	89	176	530
Polymer F	91	162	480	95	190	530

\*Comparative Example

15 Notched circumferential tensile tests

[0063] Circumferential tensile samples were cut perpendicular to the cable axis from the finished cables prepared as described above, and the notch (due to the metal overlap) was centered within the gauge length. The test was carried out as described in ASTM D638 using Die V (5) (for example microtensile), with a 2.54 cm jaw separation and pulling at 5.08 cm/minute. The results are reported in Table 3.

Table 3

Resin	Notched Tensile at 23.9°C			Notched Tensile at -32.2°C		
	Yield (kg/cm <sup>2</sup> )	Ultimate		Yield (kg/cm <sup>2</sup> )	Ultimate	
	Stress (kg/cm <sup>2</sup> )	Elongation (percent)		Stress (kg/cm <sup>2</sup> )	Elongation (percent)	
Polymer A	145	88	280	221	75	24
Polymer B	125	63	220	*a	*a	*a
Polymer C	96	79	250	211	80	180
Polymer G*	138	49	40	238	90	24
Polymer E	73	70	190	199	90	95
Polymer F	82	42	61	197	98	116

\*comparative Example

\*a : Sample Cracked

40

Reduced Notch Sensitivity (Cables)

[0064] An important aspect of the present invention is the fact that cables, where the outer cable jacket is composed of the compositions disclosed in this invention, have reduced notch sensitivity relative to comparative cable jackets. It is well known that the tensile properties of polyethylenes are sensitive to notches or surface imperfections. During the cable jacketing process, notches are generally produced at the shield overlap. In the case of poor or incomplete shield overlap, severe notches are produced in the jacket which can result in failures under relatively mild impact or tensile forces. The reduced notch sensitivity of the cable jackets of this invention is shown in Table 4. For example, due to the notch, the cable jackets of this invention lost 26 to 54 percent of their tensile elongation, that is, the tensile elongation with no notch present. In contrast, 90 percent of the tensile elongation was lost for cable jackets produced from a comparative polyethylene (Example G). Thus, cable jackets produced from the copolymers of this invention have reduced notch sensitivity. Reduced notch sensitivity means the cables are easier to install, for example, the cables do not fail (split) during the bending and/or twisting which occurs during the installation process.

55

Table 4

Sample	Percent (%)		
	Cable Jacket Circumferential Tensile Elongation	Cable Jacket Notched Circumferential Tensile Elongation	Loss of Elongation. due to Notch
Example A	380	280	26
Example B	450	220	51
Example C	540	250	54
Comparative Example G	400	40	90

15 Cable Flexibility

[0065] Cable flexibility of the final cable jacket bonded to corrugated steel was determined by measuring the amount of force required to deflect the cable. A cable having a length of 33 cm was cut, the cable core was discarded, and each end, approximately 3 cm in length, was flattened. The cable was inserted through the upper grip assembly of the Instron tensile machine and the flattened ends were clamped to the frame of the Instron tensile machine. The cable samples were deflected at a rate of 12.7 cm/minutes, and the force required to deflect the cable 5, 10, 15 and 20 mm was recorded and reported in Table 5. Lower force indicates greater flexibility. This test is described in detail in "Chemical/Moisture Barrier Cable for Underground Systems" by K.E. Bow and Joseph H. Snow, presented at IEEE/PCIC Conference, held Sept. 1981 in Minneapolis, MN, pp. 1-20, especially pages 8-10.

Table 5

Cable Sample	Polymer density (g/cm <sup>3</sup> )	Force (Kg) at Deflection of			
		5mm	10mm	15mm	20mm
Polymer A	0.958	7.3	11.5	14.6	17.2
Polymer B	0.957	6.8	11.5	14.6	16.8
Polymer C	0.952	6.3	10.4	13.5	16.8
Polymer G*	0.958	8.0	12.7	16.4	19.7
Polymer E	0.948	5.2	9.4	12.5	14.8
Polymer F	0.94	6.5	10.0	12.9	15.7

\*Comparative Example

[0066] The cables made from polymer A (density: 0.958 g/cm<sup>3</sup>), polymer B (density: 0.957 g/cm<sup>3</sup>) and polymer C (density: 0.952 g/cm<sup>3</sup>) showed greater flexibility (that is lower force at deflection) than cable made from Polymer G (density: 0.958 g/cm<sup>3</sup>), where these samples are of similar density. Especially, the cable made from polymer A showed superior flexibility than the cable made from polymer G, despite the density of the both polymers being about the same. The results for these two trials are also shown graphically in FIG. 1. The results shown in Table 5 indicate the cables of the present invention have superior flexibility than the cable made from the current polymer. For example, the data show that it takes less force to deflect a cable of the invention for a given distance (for example, 5, 10, 15 or 20 mm as shown in the table), than for a cable made from currently commercially available polyethylene, even at similar densities.

50 Shrinkback

[0067] Samples of jacket were removed from the finished cable prepared above, and the shrinkback was measured in accordance with ASTM D 4565. As an exception to ASTM D 4565, 4 specimens having 5.1 cm length parallel to the cable axis and 6.4 mm width were cut from the cable. One of the specimens was cut from a portion of the cable lying directly over the outer shield overlap and the other three were cut at successive 90 degree increments to the overlap. Cables should not shrink back more than 5 percent, preferably not more than 2 percent, after 4 hours in an oven at 100°C. The results are reported in Table 6.

## EP 0 892 979 B1

Table 6

Resin	percent Shrinkback
Polymer A	1.5
Polymer B	0.5
Polymer C	0.5
Polymer G*	1.0
Polymer E	1.0
Polymer F	1.0

\*Comparative Example

5

10

20

25

40

45

50

55

Melt Index Drift

[0068] The melt index of the cable jacket, after extrusion, was determined according to ASTM D 1238. The percent drift in melt index (that is, the change in melt index as a result of extrusion) (percent MI drift) was determined using the following equation:

$$\text{percent MI}^{\text{drift}} = (\text{MI}^{\text{cable}} - \text{MI}^{\text{initial}}) / \text{MI}^{\text{initial}}$$

wherein  $\text{MI}^{\text{initial}}$  represents a melt index of the resin prior to extrusion, and  $\text{MI}^{\text{cable}}$  represents a melt index after extrusion. The change in melt index as a result of extrusion indicates the amount of crosslinking that may take place during extrusion; normally, minimal change is desired. The results are reported in Table 7.

Table 7

Resin	$\text{MI}^{\text{cable}}$	$\text{MI}^{\text{initial}}$	percent $\text{MI}^{\text{drift}}$
Polymer A	0.83	0.78	6.4
Polymer B	0.94	0.89	5.6
Polymer C	0.96	0.87	10.3
Polymer G*	0.16	0.12	33.3
Polymer E	0.75	0.58	29.3
Polymer F	0.96	0.88	9.1

\*Comparative Example

[0069] The results shown in Table 7 indicate that the melt index drift of the resin used in the present invention was generally lower than that of commercially available currently used resin G\*.

Jacket Bond Test

[0070] The jacket bond test was conducted according to ASTM D 4565 for cables with a bonded steel sheath. A section of the cable jackets prepared as described above was removed by slitting the jacket longitudinally along the shield overlap. The cable was ringed circumferentially with a knife, flexed at the cut point to break the steel shield at the ring. The metal sheath was opened, flattened, and the cable core was discarded. The specimen strip was cut in the circumferential direction. Three strips having a width of 13 mm were cut for each strip. For each specimen, the jacket was separated from the shield or armor only of a length sufficient to permit forming a tab of each sheath component. Three specimens were tested for each cable sample at a crosshead speed of 50 mm / minute. The results are reported in Table 8.

EP 0 892 979 B1

Table 8

Resin	Circumferential		Longitudinal		Overlap
	Bond Strength (N/m)	Failure Mode	Bond Strength (N/m)	Failure Mode	
Polymer A	4,136	Jacket	6,110	Metal / Jacket	6,366
Polymer B	10,246	Jacket / Metal	7,299	Metal	3,929
Polymer G	6,523	Jacket	7,721	Metal/ Jacket	1,160
Polymer E	5,963	Metal	5,825	Metal	4,224
Polymer D	6,601	Jacket / Metal	6,110	Metal	6,091

15 Bend Tests: Hot, Room Temperature and Cold

[0071] A cold bend test was conducted according to ICEA specification S-84-608-1988 which calls out ASTM 4565 for the specifics on the test procedure. Samples were equilibrated in a cold room at -30°C for 4 hours, prior to the testing. A cable sample having length of 91.4 cm was bent in a 180° arc around a mandrel having a diameter of 8 times the cable diameter, then the sample was straightened, rotated 180°, and then bent again 180°. Upon completion of the second bend, the cable was straightened, rotated 90° and bent in a 180° arc. Upon completion of the third bend, the cable was straightened, rotated 180° and then bent for the fourth time.

[0072] A room temperature bend test was conducted in a manner similar to ASTM 4565. The cable samples were conditioned at 20°C for 4 hours prior to testing. A cable sample was bent in the same manner as the cold bend test as described above, except the sample was bent around a mandrel having a diameter of 20 times the cable diameter.

[0073] A hot bend test was conducted in a manner similar to ASTM 4565. The cable samples were conditioned at 60°C for 4 hours prior to testing. A cable sample was bent in the same manner as the cold bend test as described above, except the sample was bent around a mandrel having a diameter of 10 times that of the cable diameter.

[0074] After bending each cable sample, the surface area of the samples were inspected for cracks in the bent area using normal or corrected to normal vision. Results of the cold, room temperature and hot bend test are reported in Table 9.

Table 9

Resin	-30°C bend	20°C bend	60°C bend
Polymer A	no visual change	no visual change	no visual change
Polymer B	no visual change	no visual change	no visual change
Polymer D*	no visual change	no visual change	no visual change
Polymer E	no visual change	no visual change	no visual change
Polymer G*	no visual change	no visual change	no visual change

\*Comparative Example

45 Cold impact test.

[0075] According to ASTM D-4565, the cable samples were conditioned at -20°C for 4 hours and tested for impact resistance. A 0.45 kg weight was dropped onto the cable samples from a height of 0.9 m, and inner and outer surfaces of the cable samples were inspected with normal or corrected to normal vision. The results are reported in Table 10.

Table 10

Resin	-20°C bend
Polymer A	no visual change
Polymer B	no visual change
Polymer D*	no visual change

\*Comparative Example

EP 0 892 979 B1

Table 10 (continued)

Resin	-20°C bend
Polymer E	no visual change
Polymer G*	no visual change

\* Comparative Example

Cable Torsion

[0076] Cable samples having length of 152 cm were conditioned more than 24 hours at a temperature of 18 to 27°C. One end of the straight sample was fixed in a vise and the other end was rotated in a direction opposite to the overlap in the steel sheath without bending during the test, by an angle  $\phi$  defined below in Equation (IV),

(IV)  $\phi = 540 \cdot 3.5 / OD$

wherein OD is an outer diameter of the cable in mm. The results are reported in Table 11.

Table 11

Resin	Torsion Result
Polymer A	no visual change
Polymer B	no visual change
Polymer D*	no visual change
Polymer E	cable zippered
Polymer G*	no visual change

Example 8, 9, 10, 12 and 14, and Comparative Example 11 and 13, Abrasion Resistance

[0077] The abrasion resistance of Polymers A, B, C and F (which are the same polymers used in Examples 1, 2, 3 and 6), and Polymer H which is an *in-situ* blend produced by the same process described in Example 1 (polymer H is an ethylene/1-octene copolymer blend), are summarized in Table 13. Examples 8, 9 and 10 are summarized in Table 12. The Taber abrasion data is detailed in Table 13, which measurements were determined using abrading wheel H 18 with a 1000 g load and 1000 cycles on molded plaques.

Table 12

Example No.	Resin	$I_2$ (g/10min.)	$I_{10}/I_2$	Density (g/cm <sup>3</sup> )
Example 8	Polymer An*	0.92	11.87	0.94
Example 9	Polymer Bn*	0.89	11.35	0.94
Example 14	Polymer H**	0.82	11.45	0.952

\* "n" denotes natural version of these polymers, that is, no carbon black or fluoroelastomer

\*\* Sample contains 2.6 wt percent carbon black and 400 ppm of fluoroelastomer

Table 13

Example No.	Resin*	Taber Abrasion (g lost / 1000 revolutions)
Example 8	Polymer An	0.033
Example 9	Polymer Bn	0.031

\* "n" denotes natural version of these polymers, that is, no carbon black or fluoroelastomer

EP 0 892 979 B1

Table 13 (continued)

Example No.	Resin*	Taber Abrasion (g lost / 1000 revolutions)
Example 10	Polymer C	0.033
Comparative Example 11	Polymer G	0.029
Example 12	Polymer F	0.039
Comparative Example 12	Polymer D	0.031
Example 14	Polymer H	0.029

\* "n" denotes natural version of these polymers, that is, no carbon black or fluoroelastomer

15 [0078] As the data of Table 13 indicate, the polymer compositions disclosed in the present invention have similar abrasion resistance relative to the currently available polymers.

Examples 15, 16, 18 and 19, and Comparative Examples 17 and 20, Notch Sensitivity

20 [0079] Plaque samples for standard microtensile test according to ASTM D-1708, Die V (5) were prepared using a special mold containing four ridges with the dimensions described in Table 14. These ridges produced well defined notches in the final plaques. Microtensile dogbone samples were cut from the plaque, with the notch centered within the gauge length. The tensile test was conducted according to ASTM D 638 at 25.4 cm/minutes cross-head speed (pull rate) with 2.5 cm jaw separation at three temperatures, for example -30°C, 0°C and 25°C, using each notched sample and control samples having no notch. The results are reported in Table 15.

Table 14

	Notch Depth (mm)	Notch Radius (mm)	Radius/Depth Ratio
Notch 1	0.251	0.508	2.02
Notch 2	0.249	0.381	1.53
Notch 3	0.254	0.254	1.00
Notch 4	0.257	0.127	0.50

Table 15

Example No.	Polymer / Density (g/cm <sup>3</sup> )	Notch	Elongation at Break (percent)			Stress at Break (kg/cm <sup>2</sup> )		
			20°C	0°C	-30°C	20°C	0°C	-30°C
Example 15	Polymer B / 0.957	Control	546	452	279	229.8	237.3	231.8
		Notch 1	529	180	32	212.6	157.1	232.3
		Notch 2	230	41	24	138.7	173.9	242.6
		Notch 3	44	24	17	55.9	176.8	220.8
		Notch 4	34	20	13	52.9	150.0	220.4
Example 16	Polymer C / 0.952	Control	627	458	150	236.0	216.3	224.2
		Notch 1	439	392	26	195.0	191.0	203.8
		Notch 2	452	53	21	203.0	182.0	203.3
		Notch 3	48	26	20	75.5	183.5	211.1
		Notch 4	38	29	17	41.3	54.1	163.6

Table 15 (continued)

Example No.	Polymer / Density (g/cm <sup>3</sup> )	Notch	Elongation at Break (percent)			Stress at Break (kg/cm <sup>2</sup> )		
			20°C	0°C	-30°C	20°C	0°C	-30°C
Comparative Example 17	Polymer G / 0.958	Control	637	304	128	173.3	197.1	224.1
		Notch 1	53	25	16	109.9	73.9	276.1
		Notch 2	29	22	52	156.2	128.9	211.6
		Notch 3	20	18	52	179.4	64.8	211.4
		Notch 4	22	19	12	104.9	55.5	394.5
Example 18	Polymer E / 0.948	Control	624	505	472	252.1	284.9	299.9
		Notch 1	543	497	310	210.7	281.1	276.0
		Notch 2	508	471	30	190.6	265.9	223.5
		Notch 3	218	43	23	140.4	104.7	223.2
		Notch 4	44	35	16	53.5	67.2	241.6
Example 19	Polymer F / 0.940	Control	671	573	452	261.0	215.1	270.8
		Notch 1	574	524	326	208.4	281.2	253.4
		Notch 2	542	493	33	196.0	262.7	210.7
		Notch 3	273	45	22	128.8	127.3	216.1
		Notch 4	47	35	26	57.1	64.7	79.2
Comparative Example 20	Polymer D / 0.942	Control	923	739	372	259.7	297.6	230.1
		Notch 1	759	683	405	216.1	285.8	225.4
		Notch 2	736	653	454	209.5	277.3	242.4
		Notch 3	689	438	28	202.8	205.9	199.0
		Notch 4	71	47	19	83.2	84.1	207.1

[0080] As shown in Table 15, the polymers used in the cable of the present invention (for example polymer B, C, E and F) were less notch sensitive than the polymers currently available in the industry (for example Polymer D and G), comparing at about same density, for example, Polymers B and C have the higher elongation at break than Polymer G, and polymers E and F have the higher elongation at break than Polymer D, at almost all temperatures.

#### Reduced Notch Sensitivity (Compression Molded Plaques)

[0081] Improved notch sensitivity of the copolymers of this invention was also demonstrated by the tensile properties of compression molded plaques, as described in "Notched Tensile Low-Temperature Brittleness Test for Cable jacketing Polyethylene" by R. Bernie McAda, as appeared in the May 1983 issue of Wire Journal International Magazine. Well defined notches were produced in compression molded plaques using a special "notched" mold. In general, as shown in Figure 2, tensile elongation decreased as the severity of the notch increased (for example, Notch 2 was more severe than Notch 1, etc.). Figure 2 also shows that the copolymer described in this invention (Example B) is much less notch sensitive than comparative Example G. In fact, Notch 1 had no effect on the ultimate tensile elongation of Example B (within experimental error), while comparative Example G failed catastrophically at all four notches.

#### Improved Low Temperature Tensiles (Compression Molded Plaques)

[0082] The copolymers useful in this invention also have improved low temperature tensile properties. For example, as shown in Figure 3, the reduction in tensile elongation for Example A was 18 percent at 0°C and 56 percent at -30°C. In contrast, the reduction in tensile elongation for comparative Example G was 52 percent at 0°C and 80 percent at -30°C. Thus, relative to comparative samples, the copolymers of this invention have improved tensile properties at low

temperature. As a result, the cables of this invention are easier to install at low temperatures, for example, less susceptible to failures (splitting) at low temperatures.

5      **Claims**

1. A cable of categories 1, 2 or 3 as defined by ASTM D 1248, comprising a jacket layer comprising a polyethylene composition, **characterized in that** the polyethylene composition comprises:

10     (A) from 25 to 45 percent by weight of the total composition of at least one homogeneously branched ethylene/α-olefin interpolymer having:

- (I) a density from 0.89 g/cm<sup>3</sup> to 0.94 g/cm<sup>3</sup>,
- (II) a molecular weight distribution (Mw/Mn) from 1.8 to, less than 3.5,
- (III) a melt index, I<sub>2</sub>, from 0.001 g/10 min. to less than 0.5 g/10 min., and
- (IV) a CDBI greater than 50 percent,

20     (B) at least 5 percent by weight of the total composition of at least one heterogeneously branched ethylene interpolymer or linear ethylene homopolymer having a density from 0.9 g/cm<sup>3</sup> to 0.965 g/cm<sup>3</sup>,

25     wherein the final melt index, I<sub>2</sub>, of the polyethylene composition in the cable jacket is in the range from 1 to 50 g/10 minutes, the polyethylene composition has a density of 0.945 g/cm<sup>3</sup> or more, and the cable jacket has a strain hardening modulus, G<sub>p</sub>, greater than 1.6 MPa wherein G<sub>p</sub> is calculated according to the following equation:

$$G_p = \frac{\sigma_{dr} \lambda_n - \sigma_{dr}}{\lambda_n^2 \cdot \frac{1}{\lambda_n}},$$

30     wherein λ<sub>n</sub> and σ<sub>dr</sub> represent the natural draw ratio and engineering draw stress, respectively, and a reduced notch sensitivity as indicated for a notched cable jacket comprising a polyethylene composition and having a thickness from 2.03 to 2.29 mm (80-90 mil) taken in a circumferential direction by less than 55% loss of elongation compared to an unnotched cable jacket sample from said cable, as measured in accordance with ASTM D 638 at 23.9°C using a die V (5) with a 2.5 cm jaw separation and pulling at a rate of 5.08 cm per minute.

2. The cable according to Claim 1 wherein the at least one homogeneously branched ethylene/α-olefin interpolymer of part (A) of Claim 1 is a substantially linear ethylene polymer having long chain branching or a linear ethylene polymer having an absence of long chain branching.

3. The cable according to any one of the preceding claims wherein the polyethylene composition is further **characterized by** having a melt flow ratio, I<sub>10</sub>/I<sub>2</sub> from 7.0 to 16.0.

4. The cable of any of the preceding claims wherein the at least one heterogeneously branched ethylene interpolymer is at least one interpolymer of ethylene with at least one C<sub>3</sub>-C<sub>20</sub> α-olefin.

5. A cable according to any of the preceding claims comprising a layer of a polyethylene composition **characterized in that** the polyethylene composition comprises:

50     (A) 40 percent of at least one ethylene/α-olefin interpolymer having:

- (I) a density from 0.91 to 0.92 g/cm<sup>3</sup>,
- (II) a molecular weight distribution (Mw/Mn) of 2,
- (III) a melt index, I<sub>2</sub>, of 0.1 g/10 min., and
- (IV) a CDBI greater than 50 percent,

(B) 60 percent by weight of the total composition of at least one heterogeneously branched ethylene/α-olefin interpolymer having:

- 5 (I) a density of 0.96 g/cm<sup>3</sup>,
- (II) a melt index, I<sub>2</sub>, of 6 g/10 min., and
- (III) a CDBI less than 50 percent.

6. The cable according to Claim 1 wherein the polyethylene composition is prepared by a process comprising the steps of:

- 10 (i) reacting by contacting ethylene and at least one α-olefin under solution polymerization conditions in at least one reactor to produce a solution of the at least one homogeneously branched ethylene/α-olefin interpolymer of Claim 1,
- 15 (ii) reacting by contacting ethylene and at least one α-olefin under solution polymerization conditions in at least one other reactor to produce a solution of the at least one heterogeneously branched ethylene interpolymer of Claim 1,
- (iii) combining the solution of the at least one homogeneously branched ethylene/α-olefin interpolymer prepared in the step (i) and the solution of the at least one heterogeneously branched ethylene interpolymer prepared in the step (ii), and
- 20 (iv) removing the solvent from the polymer solution of step (iii) and recovering the polyethylene composition.

7. The cable according to any of the preceding claims, wherein the polyethylene composition is thermoplastic and a plaque, having

25 a single notch and a thickness from 1.78-2.03 mm. (70 to 80 mils), made from said polyethylene composition has at least 100 percent ultimate tensile elongation, wherein the notch has a depth of 0.25 mm. (10 mils) or more and a radius from 0.275 mm to 0.55 mm.

8. The cable according to Claim 8, wherein the ultimate elongation is at least 200 percent.

### 30 Patentansprüche

1. Kabel der Kategorien 1, 2 oder 3, wie es durch ASTM D 1248 definiert ist, umfassend eine Mantelschicht umfassend eine Polyethylen-Zusammensetzung, dadurch gekennzeichnet, dass die Polyethylen-Zusammensetzung umfasst:

(A) 25 bis 45 Gew.-% mindestens eines homogen verzweigten Ethylen/α-Olefin-Interpolymers, bezogen auf die Gesamtzusammensetzung, mit:

- 40 (i) einer Dichte von 0,89 g/cm<sup>3</sup> bis 0,94 g/cm<sup>3</sup>,
- (ii) einer Molekulargewichtsverteilung (M<sub>w</sub>/M<sub>n</sub>) von 1,8 bis weniger als 3,5,
- (iii) einem Schmelzindex, I<sub>2</sub>, von 0,001 g/10 min bis weniger als 0,5 g/10 min, und
- (iv) einem CDBI von größer als 50 Prozent,

45 (B) mindestens 5 Gew.-% mindestens eines heterogen verzweigten Ethylen-Interpolymers oder linearen Ethylen-Homopolymers, bezogen auf die Gesamtzusammensetzung, mit einer Dichte von 0,9 g/cm<sup>3</sup> bis 0,965 g/cm<sup>3</sup>,

50 wobei der End-Schmelzindex, I<sub>2</sub>, der Polyethylen-Zusammensetzung in dem Kabelmantel im Bereich von 1 bis 50 g/10 Minuten liegt, die Polyethylen-Zusammensetzung eine Dichte von 0,945 g/cm<sup>3</sup> oder mehr aufweist und der Kabelmantel einen Umformverfestigungsmodul, G<sub>p</sub>, von größer als 1,6 MPa aufweist, wobei G<sub>p</sub> gemäß folgender Gleichung berechnet wird:

$$55 G_p = \frac{\sigma_d \lambda_n - \sigma_{dr}}{\lambda_n^2 - \frac{1}{\lambda_n}},$$

EP 0 892 979 B1

worin  $\lambda_n$  und  $\sigma_{dr}$  das natürliche Ziehverhältnis bzw. die technische Ziehspannung darstellen, und eine verringerte Kerbempfindlichkeit von weniger als 55 % Dehnungsverlust, angegeben für einen gekerbten Kabelmantel, umfassend eine Polyethylen-Zusammensetzung und mit einer Dicke von 2,03 bis 2,29 mm (80-90 Mil), in Umfangsrichtung aufweist, verglichen mit einer ungekerbten Kabelmantel-Probe des Kabels, gemessen gemäß ASTM D 638 bei 23,9 °C unter Verwendung einer Matrize V (5) mit einer Backenseparation von 2,5 cm und einer Ziehrate von 5,08 cm pro Minute.

5 2. Kabel nach Anspruch 1, wobei das mindestens eine homogen verzweigte Ethylen/α-Olefin-Interpolymer aus Teil (A) in Anspruch 1 ein im Wesentlichen lineares Ethylen-Polymer mit Langkettenverzweigung oder ein lineares Ethylen-Polymer ohne Langkettenverzweigung ist.

10 3. Kabel nach einem der vorhergehenden Ansprüche, wobei die Polyethylen-Zusammensetzung ferner dadurch gekennzeichnet ist, dass sie ein Schmelzfluss-Verhältnis,  $I_10/I_2$ , von 7,0 bis 16,0 aufweist.

15 4. Kabel nach einem der vorhergehenden Ansprüche, wobei das mindestens eine heterogen verzweigte Ethylen-Interpolymer mindestens ein Interpolymer von Ethylen mit mindestens einem C<sub>3</sub>-C<sub>20</sub>-α-Olefin ist.

20 5. Kabel nach einem der vorhergehenden Ansprüche, umfassend eine Schicht einer Polyethylen-Zusammensetzung, dadurch gekennzeichnet, dass die Polyethylen-Zusammensetzung umfasst:

(A) 40% mindestens eines Ethylen/α-Olefin-Interpolymers mit:

- 25 (i) einer Dichte von 0,91 bis 0,92 g/cm<sup>3</sup>,  
(ii) einer Molekulargewichtsverteilung ( $M_w/M_n$ ) von 2,  
(iii) einem Schmelzindex,  $I_2$ , von 0,1 g/10 min, und  
(iv) einem CDBI von größer als 50 Prozent,

30 (B) 60 Gew.-% mindestens eines heterogen verzweigten Ethylen/α-Olefin-Interpolymers, bezogen auf die Gesamtzusammensetzung, mit:

- (i) einer Dichte von 0,96 g/cm<sup>3</sup>,  
(ii) einem Schmelzindex,  $I_2$ , von 6 g/10 min, und  
(iii) einem CDBI von weniger als 50 Prozent.

35 6. Kabel nach Anspruch 1, wobei die Polyethylen-Zusammensetzung durch ein Verfahren hergestellt ist, das die Schritte umfasst:

40 (i) Umsetzung, indem Ethylen und mindestens ein α-Olefin unter Lösungspolymerisationsbedingungen in mindestens einem Reaktor in Kontakt gebracht werden, um eine Lösung des mindestens einen homogen verzweigten Ethylen/α-Olefin-Interpolymers gemäß Anspruch 1 herzustellen,

45 (ii) Umsetzung, indem Ethylen und mindestens ein α-Olefin unter Lösungspolymerisationsbedingungen in mindestens einem anderen Reaktor in Kontakt gebracht werden, um eine Lösung des mindestens einen heterogen verzweigten Ethylen-Interpolymers gemäß Anspruch 1 herzustellen,

50 (iii) Vereinigen der in Schritt (i) hergestellten Lösung des mindestens einen homogen verzweigten Ethylen/α-Olefin-Interpolymers und der in Schritt (ii) hergestellten Lösung des mindestens einen heterogen verzweigten Ethylen-Interpolymers, und

55 (iv) Entfernen des Lösungsmittels von der Polymer-Lösung aus Schritt (iii) und Gewinnung der Polyethylen-Zusammensetzung.

7. Kabel nach einem der vorhergehenden Ansprüche, wobei die Polyethylen-Zusammensetzung thermoplastisch und eine Platte ist, mit einer einzigen Kerbe und einer Dicke von 1,78-2,03 mm (70-80 Mil), hergestellt aus der Polyethylen-Zusammensetzung mit mindestens 100 Prozent Grenzzugdehnung, wobei die Kerbe eine Tiefe von 0,25 mm (10 Mil) oder mehr und einen Radius von 0,275 mm bis 0,55 mm aufweist.

8. Kabel nach Anspruch 7, wobei die Grenzdehnung mindestens 200 Prozent beträgt.

**Revendications**

1. Câble de catégorie 1, 2 ou 3 comme défini par ASTM D 1248, comprenant une couche de gainage comportant une composition de polyéthylène, **caractérisée en ce que la composition de polyéthylène comporte :**

5 (A) de 25 à 45 pour cent en poids de la composition totale d'au moins un copolymère éthylène/α-oléfine ramifié de manière homogène ayant :

- 10 (i) une masse volumique de 0,89 g/cm<sup>3</sup> à 0,94 g/cm<sup>3</sup>,  
(ii) une distribution de poids moléculaire ( $M_w/M_n$ ) de 1,8 à moins de 3,5,  
(iii) un indice de viscosité à chaud,  $I_2$ , de 0,001 g /10 min à moins de 0,5 g /10 min, et  
(iv) un CDBI supérieur à 50 pour cent,

15 (B) au moins 5 pour cent en poids de la composition totale d'au moins un copolymère d'éthylène ramifié de manière hétérogène ou un homopolymère d'éthylène linéaire ayant une masse volumique de 0,9 g/cm<sup>3</sup> à 0,9165 g/cm<sup>3</sup>

20 où l'indice de viscosité à chaud final,  $I_2$ , de la composition de polyéthylène dans la gaine de câble est dans la gamme de 1 à 50 g/10 min, la composition de polyéthylène a une masse volumique de 0,945 g/cm<sup>3</sup> ou plus, et la gaine de câble a un module de durcissement à froid,  $G_p$ , supérieur à 1,6 MPa où  $G_p$  est calculé en conformité avec l'équation suivante :

$$25 G_p = \frac{\sigma_{dr} \lambda_n - \sigma_{dr}}{\lambda_n^2 - \frac{1}{\lambda_n}}$$

30 dans laquelle  $\lambda_n$  et  $\sigma_{dr}$  représentent le rapport d'étirage naturel et la contrainte d'étirage d'ingénierie, respectivement, et une sensibilité à l'entaille réduite comme indiquée pour une gaine de câble entaillée comportant une composition de polyéthylène et ayant une épaisseur de 2,03 à 2,29 mm (80 à 90 mil) prise dans une direction circonférentielle de moins de 55 % de perte d'allongement par rapport à un échantillon de gaine de câble non entaillé dudit câble, comme mesuré en conformité avec ASTM -D 638 à 23,9 °C en utilisant une filière V(5) avec une séparation de mâchoires de 2,5 cm et une traction à une vitesse de 5,08 cm par minute.

35 2. Câble selon la revendication 1 dans lequel au moins un copolymère éthylène/α-oléfine ramifié de manière homogène de la partie (A) de la revendication 1 est un polymère d'éthylène sensiblement linéaire ayant une ramifications à longue chaîne ou un polymère d'éthylène linéaire ayant une absence de ramifications à longue chaîne.

40 3. Câble selon l'une quelconque des revendications précédentes, dans lequel la composition de polyéthylène est, en outre, **caractérisée par** le fait d'avoir un rapport d'indices de viscosité à chaud,  $I_{10}/I_2$  de 7,0 à 16,0.

45 4. Câble selon l'une quelconque des revendications précédentes, dans lequel au moins un copolymère d'éthylène ramifié de manière hétérogène est au moins un copolymère d'éthylène avec au moins une α-oléfine en C<sub>3</sub> à C<sub>10</sub>.

5. Câble selon l'une quelconque des revendications précédentes, comportant une couche d'une composition de polyéthylène, **caractérisé en ce que la composition de polyéthylène comporte :**

(A) 40 pour cent d'au moins un copolymère éthylène/ α - oléfine ayant :

- 50 (i) une masse volumique de 0,91 à 0,92 g/cm<sup>3</sup>,  
(ii) une distribution de poids moléculaire ( $M_w/M_n$ ) de 2,  
(iii) un indice de viscosité à chaud,  $I_2$ , de 0,1 g /10 min, et  
(iv) un CDBI supérieur à 50 pour cent,

55 (B) 60 pour cent en poids de la composition totale d'au moins un copolymère éthylène/α-oléfine ramifié de manière hétérogène ayant :

- (i) une masse volumique de 0,96 g /cm<sup>3</sup>,

**EP 0 892 979 B1**

(ii) un indice de viscosité à chaud,  $I_2$ , de 6 g/10 min, et  
(iii) un CDBI inférieur à 50 pour cent.

5     6. Câble selon la revendication 1, dans lequel la composition de polyéthylène est préparée par un procédé comprenant les étapes consistant à :

10    (i) faire réagir par mise en contact de l'éthylène et au moins une  $\alpha$ -oléfine sous des conditions de polymérisation en solution dans au moins un réacteur pour produire une solution du au moins un copolymère éthylène/ $\alpha$ -oléfine ramifié de manière homogène selon la revendication 1,  
15    (ii) faire réagir par mise en contact de l'éthylène et au moins une  $\alpha$ -oléfine sous des conditions de polymérisation en solution dans au moins un autre réacteur pour produire une solution du au moins un copolymère d'éthylène ramifié de manière hétérogène selon la revendication 1,  
15    (iii) combiner la solution du au moins un copolymère éthylène/ $\alpha$ -oléfine ramifié de manière homogène préparé dans l'étape (i) et la solution du au moins un copolymère d'éthylène ramifié de manière hétérogène préparée dans l'étape (ii), et  
15    (iv) enlever le solvant de la solution de polymères de l'étape (iii) et récupérer la composition de polyéthylène.

20    7. Câble selon l'une quelconque des revendications précédentes, dans lequel la composition de polyéthylène est thermoplastique et une plaque, ayant une entaille unique et une épaisseur de 1,78 à 2,03 mm (70 à 80 mil), faite de ladite composition de polyéthylène a au moins 100 pour cent d'allongement à la traction à la rupture, où l'entaille ayant une profondeur de 0,25 mm (10 mils) ou plus et un rayon de 0,275 mm à 0,55 mm.

25    8. Câble selon la revendication 7, dans lequel l'allongement à la rupture est d'au moins 200 pour cent.

30

35

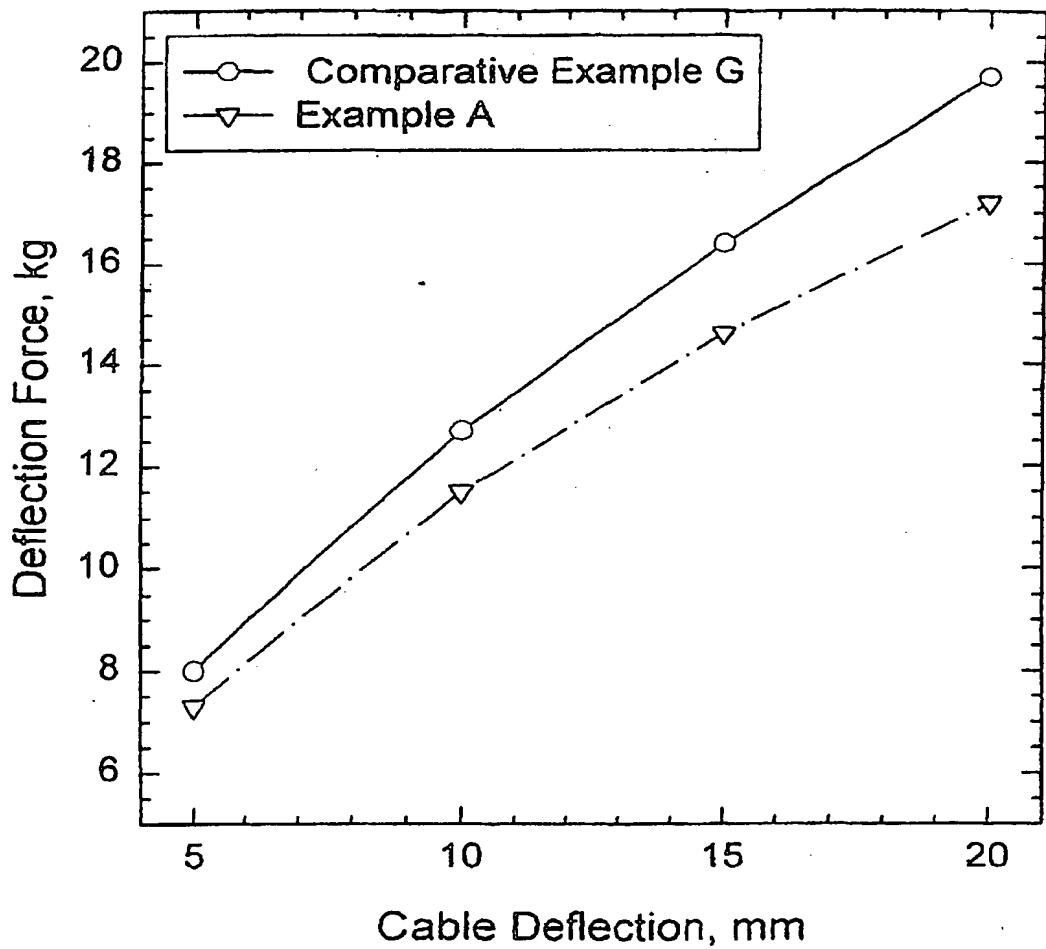
40

45

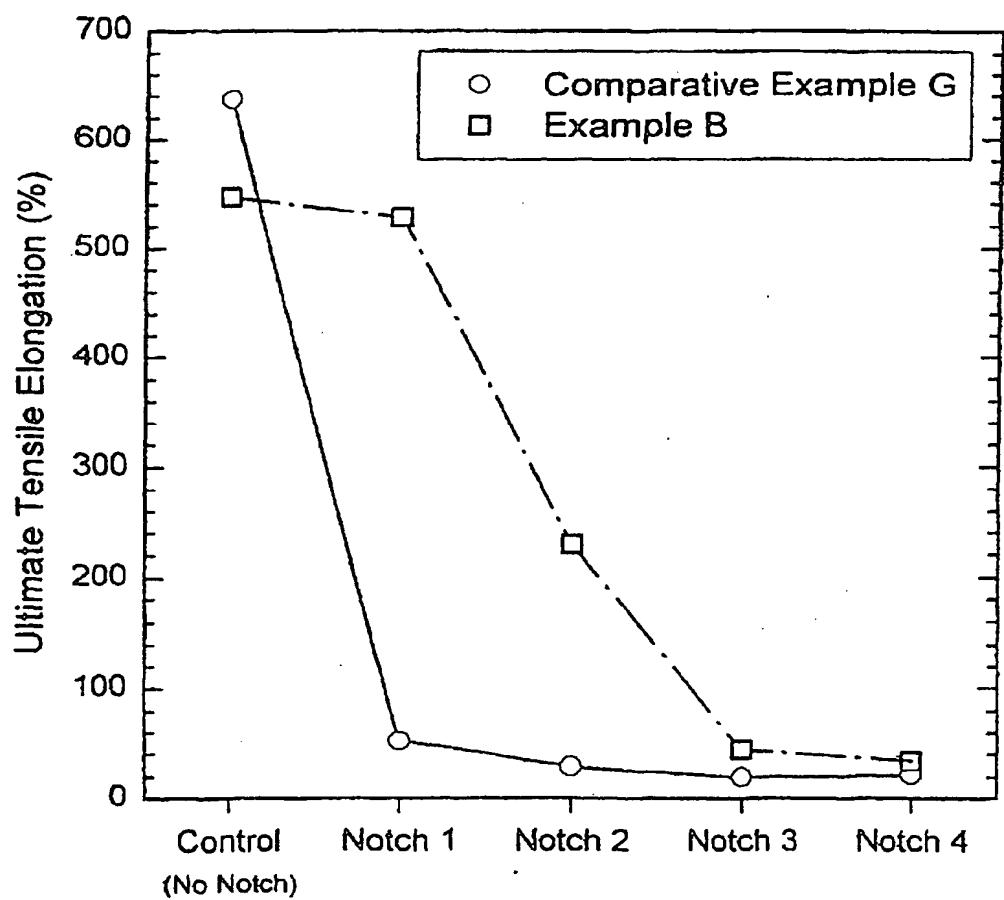
50

55

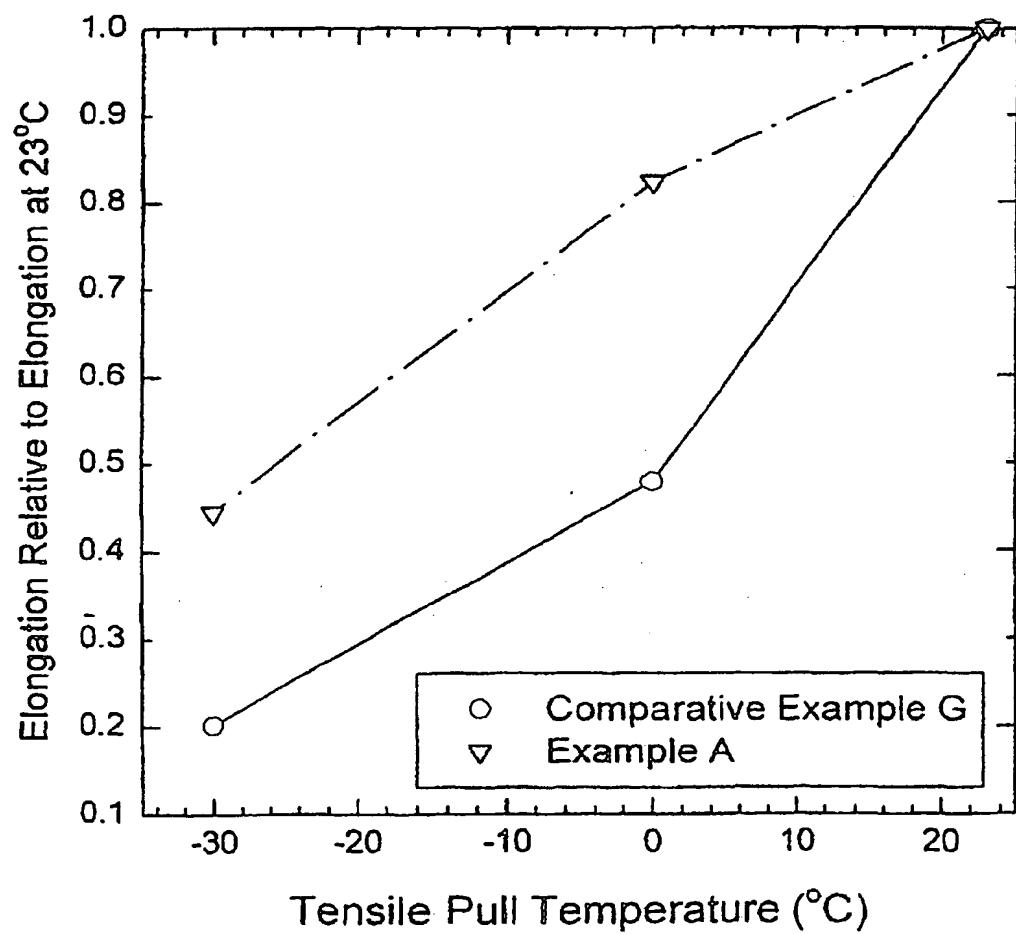
FIG. 1  
Cable Flexibility



**FIG. 2**  
Notch Sensitivity: Ultimate Tensile Elongation  
(pull rate 25.4 cm/min, room temperature)



**FIG.3**  
Relative Reduction in Tensile Elongation  
with Decreasing Temperature



**FIG. 4**  
**Tensile Strain Hardening Modulus**  
**Tensile Pulls at (5.08 cm/min)**

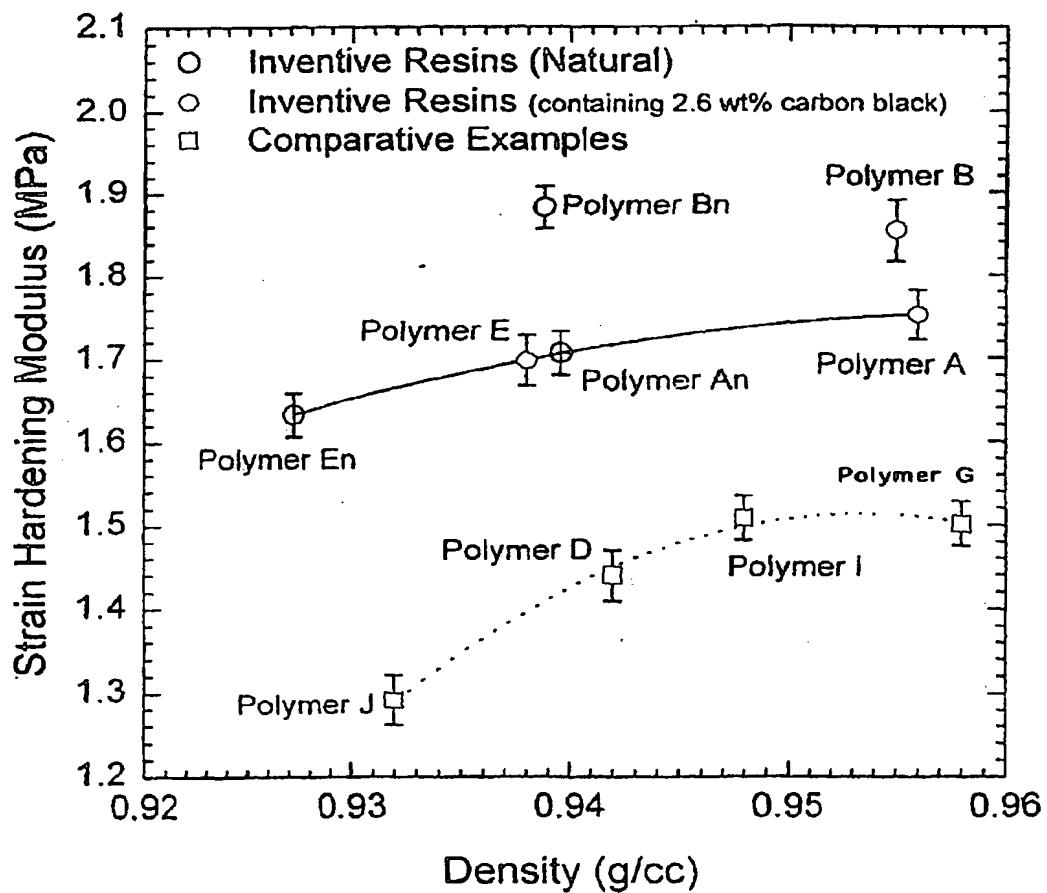


FIG.5

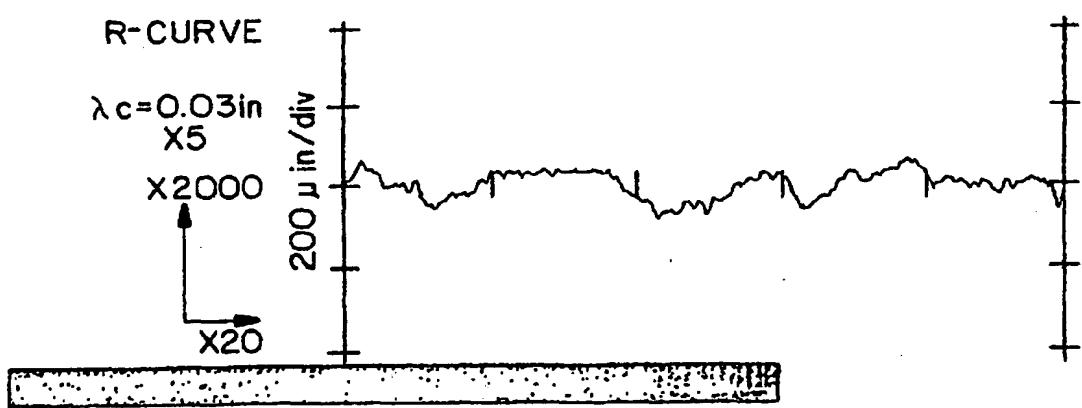


FIG.6

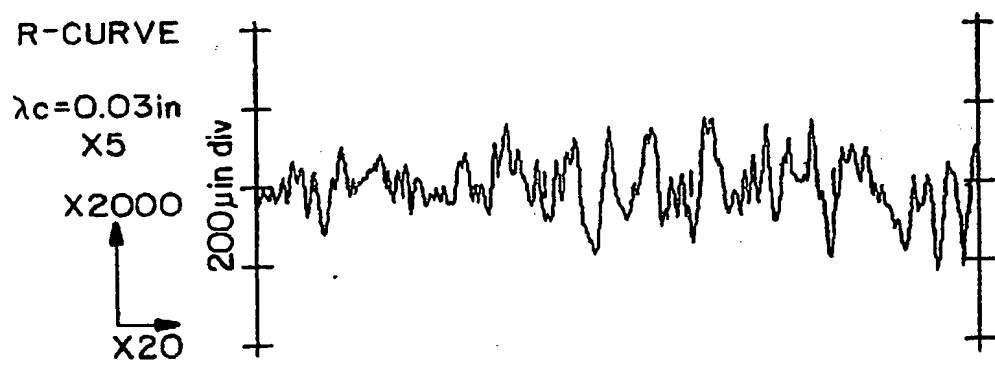


FIG. 7

